Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 78 (4) 537–548 (2013)
JSCS–4436
UDC 547.978+666.122.3:543.552+544.6.076.32–039.26
Original scientific paper

Differential pulse anodic stripping voltammetric determination of berberine using a nano-Na-montmorillonite clay-modified carbon paste electrode

WEN CHEN, MING-XIAO ZHANG*, CONG LI and YONG-LING LI

School of Chemistry and Chemical Engineering, Southwest University, 2 Rd Tiansheng, Beibei District, Chongqing, P. R. China

(Received 27 May, revised 16 July 2012)

Abstract: A simple and sensitive method is presented for the electrochemical determination of berberine based on a nano-Na-montmorillonite (nano-Na-MMT) clay-modified carbon paste electrode. The electrochemical oxidation and adsorption behavior of berberine was studied at the proposed electrode by linear sweep voltammetry in acetate buffer (0.2 M, pH 5.6). A differential pulse anodic stripping voltammetric procedure was developed for the determination of the drug. A good linear relationship between the oxidation peak current magnitude and the concentration of berberine was observed in the range from 1.0 to 18.0 μg mL^{-1} with a detection limit of 0.07 μg mL^{-1} and a quantification limit of 0.24 μg mL^{-1}. The proposed method was successfully applied to the determination of berberine in pharmaceutical tablets.

Keywords: berberine; nano-Na-montmorillonite clay; carbon paste electrode; modified electrode; electrochemical determination.

INTRODUCTION

Berberine, a well-known natural isoquinoline alkaloid, is mainly isolated from the roots and rhizomes of several plants, such as berberidaceae, ranunculaceae, menispermaceae, *etc*.[1] As a medicinal drug, it has drawn extensive attention for a long time due to its extensive biological activities, such as antibacterial,[2] antiparasitic,[3] antimicrobial,[4] antifungal,[5] hypotensive,[6] *etc*. Hitherto, numerous efforts focused on the research and development of berberine as an antimicrobial drug in the treatment of ocular trachoma infections and intestinal infections, such as acute gastroenteritis and bacillary dysentery.[4] In addition, the effects of berberine on human malignant brain tumor,[7] esophageal cancer,[8] leukemic cancer[9] and colon cancer[10] cell lines were tested and significant cell death

* Corresponding author. E-mail: pclab@swu.edu.cn
doi: 10.2298/JSC120527093C

effects were evidenced. Therefore, berberine research is becoming increasingly active with the aim of extending its possible potential in clinical practice.

Medicinal analysis plays an important role in quality control in medicine. The development of sensitive, simple, rapid and reliable methods for the determination of active ingredients is very important and interesting. At present, the methods of detection of berberine mainly include: supercritical fluid chromategraphy (SFC),[11] high performance capillary electrophoresis (HPCE),[12] thin layer chromatography (TLC),[13] electro-generated chemiluminescence (ECL),[14] resonance Raleigh scattering (RRS),[15] high performance liquid chromatography (HPLC)[16] or reverse phase liquid chromatography (RPLC)[17] and ^{1}H-NMR spectroscopy.[18] Most of these methods are costly and require expertise in addition to time-consuming pretreatment steps. The electrochemical properties of berberine have been known for a long time through studies concerned with the electrochemical reduction and adsorption of berberine at mercury electrodes.[19,20] The electrochemical reduction of berberine with a glassy carbon electrode was also reported.[21]

The carbon paste electrode (CPE), a mixture of conducting graphite powder and hydrophobic adhesive, has been extensively used in electro-analytical chemistry because of its excellent properties: wide potential range (from –1.40 to 1.30 V), easy preparation, convenient surface renewal, low residual current, porous surface, and low cost.[22] Recently, some new reports have appeared on the application of carbon paste electrodes for the analysis of drugs,[23,24] biomolecules,[25,26] and other important compounds.[27,28] These studies showed that the sensitivity of a bare CPE is relatively poor in trace assays. In order to improve its sensitivity, it is a fascinating and effective way to modify bare CPE by mixing with some other unique substances.

Nano-materials, defined as having one or more external dimension in the size range 1–100 nm, have received steadily growing interests because of their peculiar and fascinating properties, which include the quantum size effect, the small bulk effect, the surface effect and the macroscopic quantum tunneling effect.[29] Recently, some nano-materials were used as modifiers to improve the sensitivity of electrodes, such as carbon nanotubes,[23,24,27,30] gold nanoparticles,[31] SiO_2,[32] montmorillonite[33] and TiO_2.[30]

Montmorillonite belongs to the smectite group of clays and has a well-layered structure. Its predominant properties are its huge cationic exchange capacity, due to an excess negative charge on the surface of the clay, and a strong adsorptive ability, attributed to the expandability of its internal layers.[34] Therefore, montmorillonite has been widely used to modifying electrodes to improve their determination sensitivity towards anions,[35] cations,[33] and organic compounds,[36,37] and has been employed to fabricate biosensors.[38]

In this work, because of its positive charge in solution, the electrochemical oxidation and adsorption behavior of berberine were investigated using a carbon paste electrode modified with nano-Na-montmorillonite clay (nano-Na-MMT/ /CPE). A differential pulse anodic stripping voltammetric (DPASV) method was developed using acetate buffer (0.2 M, pH 5.6) as the supporting electrolyte. The proposed method was applied to the determination of the drug berberine in pharmaceutical tablets.

EXPERIMENTAL

Reagents and chemicals

Nano-Na-MMT clay (≈25 nm) was purchased from the Fenghong Clay Chemicals Co., Ltd. (Zhejiang, China). The content of montmorillonite was 96.0–98.0 %, and the apparent density and diameter thickness ratio of the material were 0.25–0.35 g cm^{-3} and 200, respectively. Berberine chloride was provided by the College of Pharmacy of the Southwest University (Chongqing, China). The analyzed formulation was "compound berberine tablets" labeling to contain 30 mg berberine chloride per tablet (Chongqing Tongjunge Pharmaceutical Factory Co., Ltd. of the Taiji Group, China).

A standard stock solution of 0.20 mg mL^{-1} berberine was prepared in ultra pure water. The desired concentration of berberine was obtained by direct dilution of the appropriate quantity of stock solution with the supporting electrolyte.

Britton–Robinson (B–R) universal buffer (pH 2–10) and acetate buffer (0.2 M, pH 3.7––5.6) were prepared in ultra pure water and were used as supporting electrolytes. All the employed chemicals were of analytical reagent grade and used without further purification.

Apparatus

All electrochemical measurements were performed on a LK2006AZ electrochemical analyzer (Lanlike Chemistry & Electron High Technology Co., Ltd. Tianjing, China). A conventional three-electrode system, including a nano-Na-MMT/CPE (3 mm in diameter), a saturated calomel reference electrode (SCE), and a platinum flat counter electrode, was employed. All potentials are referred to SCE.

Preparation of the nano-Na-MMT/CPE

Graphite powder (4.75 g) and nano-Na-MMT clay (0.25 g) were mixed uniformly by milling in a small agate mortar. Then 1.8 mL Nujol oil (d = 0.84 g mL^{-1}) and a little ethanol were added, and the mixture was milled again to obtain a homogenous 5 mass % nano-Na--MMT modified carbon paste after ethanol evaporation. Various modified carbon paste containing different mass percentages of nano-Na-MMT clay (0.0, 2, 4, 6, 8 and 10 mass %) were prepared in the same way. An amount of the prepared modified carbon paste was pressed into the end cavity of the electrode body. The surface of the constructed nano-Na-MMT/CPE was polished on clean paper before use.

General analytical procedure

Acetate buffer solution (10 mL, 0.2 M, pH 5.6) was introduced into the electrolysis cell and then a polished nano-Na-MMT/CPE was immersed in the supporting electrolyte. Then several cyclic voltammetric sweeps were applied to obtain a low background current. Then an analyte solution was introduced into the electrolysis cell, then at a selected preconcentration potential, accumulated to the developed nano-Na-MMT/CPE for a selected preconcentration time while the solution was stirred at 700 rpm. At the end of the preconcentration time, the

stirring was stopped 5 s for the solution becoming quiescent. The voltammograms were then recorded by scanning the potential in the positive direction using differential pulse voltammetry. After each measurement, the used carbon paste was carefully removed and a new nano--Na-MMT/CPE made again.

RESULTS AND DISCUSSION

Electrochemical behavior of berberine at CPE

Linear sweep voltammograms (LSV) of 10.0 μg mL^{-1} berberine were recorded at both a bare CPE and a 5 mass % nano-Na-MMT/CPE in B–R universal buffer (pH 2–10) and in acetate buffer (0.2 M, pH 3.7–5.6) at 50 mV s^{-1} before preconcentration and after preconcentration at 0.40 V for 150 s. The obtained LSVs are presented in Fig. 1. As shown, a very ill defined anodic peak was observed at the bare CPE before preconcentration (Fig. 1A, curve a), and a somewhat better peak was observed at the 5 mass % nano-Na-MMT/CPE (Fig. 1B, curve a) in acetate buffer (0.2 M, pH 5.6). The observed anodic peak corresponded to the oxidation of the methylenedioxy ring of berberine (Scheme 1).[39]

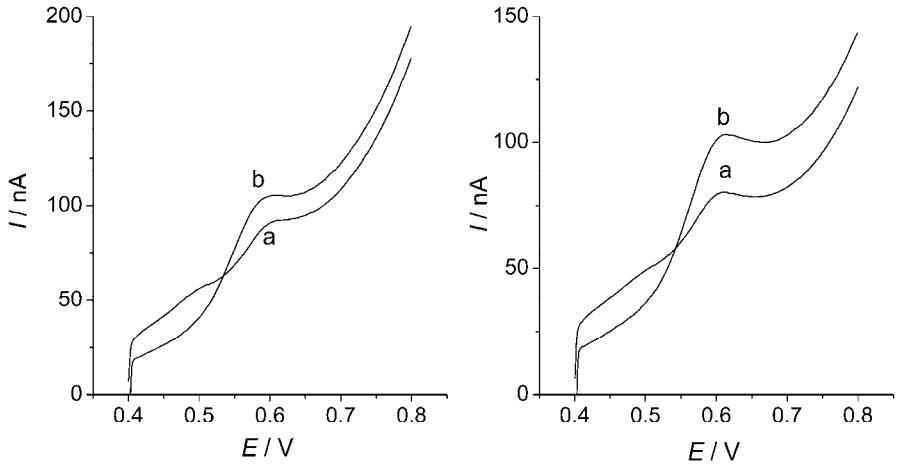
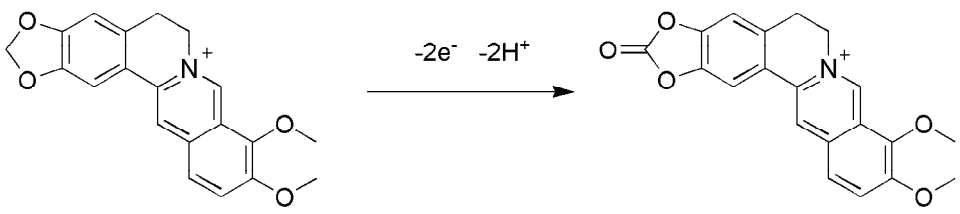


Fig. 1. Linear sweep voltammograms of 10.0 μg mL^{-1} berberine in acetate buffer (0.2 M, pH 5.6), recorded at a bare CPE (A) and at a nano-Na-MMT/CPE (B) before preconcentration (curves a) and after preconcentration at 0.40 V for 150 s (curves b), scan rate v = 50 mV s^{-1}.



Scheme 1. Proposed mechanism for the electro-oxidation of berberine.

On the other hand, the voltammograms recorded after preconcentration at 0.40 V for 150 s showed a little enhanced peak at the bare CPE (Fig. 1A, curve b) and a better-defined enhanced peak at the 5 % (w/w) nano-Na-MMT/CPE (Fig. 1B, curve b). This enhancement of the peak current compared to that at the bare CPE indicated the strong enrichment behavior of berberine onto the modified CPE. This phenomenon may be attributed to cationic exchange and the adsorptive properties of the nano-Na-MMT clay, and consequentially the sensitivity of assay for berberine was remarkably improved. Therefore, nano-Na-MMT/CPE was used as the working electrode for the rest of the analytical study.

Further, linear sweep voltammograms of 10.0 μg mL^{-1} berberine were recorded at different scan rates, v (10–300 mV s^{-1}), at the developed 5 mass % nano-Na-MMT/CPE following preconcentration at 0.40 V for 150 s. The peak current (I_p) magnitude increased upon increasing the scan rate (v). According to the simplified Randles–Sevcik equation ($I_p = -\text{constant} \times v^{1/2}$),[40] a linear plot of log I_p *vs*. log v was obtained with corresponding equation:

$$\log I_p \text{ (nA)} = 0.614 \log v + 0.692 \ (r = 0.998 \text{ and } n = 7)$$

where v is in mV s^{-1}. The slope value of 0.614 is close to the expected theoretical value of 0.5, indicating that the oxidation process of berberine at a nano-Na-MMT/CPE is diffusion controlled. Moreover, as the scan rate was increased, the peak potential (E_p) shifted towards more positive potential, showing an irreversible oxidation process.[41] Since a slope value of 0.256 V dec^{-1} was found from the Tafel plot constructed from data of the rising part of the current–voltage curve recorded at a scan rate of 50 mV s^{-1}, it could be estimated that $\alpha n_a = 1.05$. The number of electrons, n_a, transferred in the rate-determining step of the removal of electrons from the methylenedioxy ring of the berberine moiety was 2.[39] Then, the transfer coefficient α should be 0.52.

Based on the electrochemical oxidation and the adsorption behavior of berberine onto the developed nano-Na-MMT/CPE surface, a differential pulse anodic stripping voltammetric (DPASV) method was optimized for its trace determination.

Composition and stability of the nano-Na-MMT/CPE

DPASV curves of 10.0 μg mL^{-1} berberine in acetate buffer (0.2 M, pH 5.6) at CPEs modified with various mass percentages (% w/w) of nano-Na-MMT clay were recorded after preconcentration at 0.20 V for 150 s. As shown in Fig. 2, the magnitude of the peak current (I_p) increased with increasing percentage of nano-Na-MMT clay in the modified CPE up to 5 mass %, and then decreased. Such an enhancement of the magnitude of stripping peak current (I_p) was expressed due to the strong adsorptive properties of the nano-Na-MMT clay. However, at higher percentage of nano-Na-MMT clay in the modified CPE, the decrease in the magnitude of the peak current (I_p) may be attributed to the decrease in conductivity of

the electrode with the increasing percentage of the nonconductive nano-Na-MMT clay, which hindered the electron transfer process and increased the background current. This status reflected the competitive relationship between the adsorption ability and the conductive ability of the electrode. As stated above, 5 mass % of nano-Na-MMT/CPE was used in the succedent analytical study.

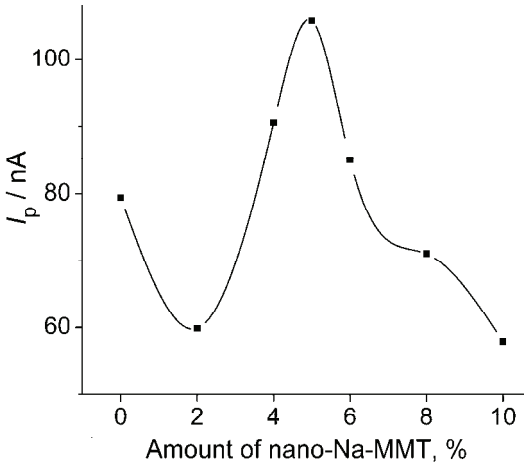


Fig. 2. Effect of the mass percentage (% w/w) of nano-Na-MMT clay on the DPASV peak current (I_p) of 10.0 μg mL^{-1} berberine in acetate buffer (0.2 M, pH 5.6); E_{acc} = 0.20 V, t_{acc} = 150 s, ΔE_s = 6 mV, E_a = 100 mV, t_w = 0.1 s and t_p = 0.5 s.

Moreover, the reproducibility of results utilizing 5 mass % nano-Na-MMT/ /CPE fabricated repeatedly was examined by comparing the DPASV oxidation peak current (I_p) of 10.0 μg mL^{-1} berberine. Nine repetitive analyses utilizing three separately fabricated 5 mass % nano-Na-MMT/CPE were obtained. It was found that the oxidation peak current (I_p) magnitude remained almost constant with a relative standard deviation of 4.2 %.

SEM characterization of the surface of the electrodes

Figure 3 depicts the typical images of scanning electronic microscope (SEM) based on different electrodes. Figure 3A shows an obvious image of the smooth graphite layer. After mixed nano-Na-MMT and graphite powder, a homogeneous morphology was obtained with a loose and porous layer (Fig. 3B).

Pulse parameters and preconcentration parameters

DPASV of 10.0 μg mL^{-1} berberine in acetate buffer (0.2 M, pH 5.6) following its preconcentration onto a developed 5 mass % nano-Na-MMT/CPE at 0.20 V for 150 s were recorded at the various pulse parameters (scan-increment ΔE_s = = 2–15 mV, pulse-amplitude E_a = 5–100 mV, pulse-width t_w = 0.01–1 s, and pulse-period t_p = 0.1–1 s). A developed, obvious and symmetrical voltammetric peak was obtained under the following pulse parameters: ΔE_s = 6 mV, E_a = 100 mV, t_w = 0.1 s and t_p = 0.5 s.

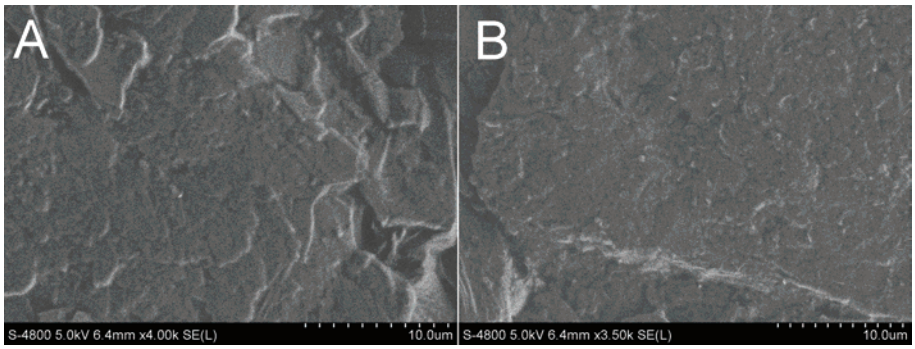


Fig. 3. SEM Images of a bare CPE (A) and a 5 mass % nano-Na-MMT/CPE (B).

The effect of various preconcentration potentials (E_{acc}) from −0.30 to 0.40 V on the magnitude of the peak current (I_p) of the DPASV of 10.0 μg mL^{-1} berberine in acetate buffer (0.2 M, pH 5.6) was evaluated at a 5 mass % nano-Na--MMT/CPE following preconcentration for 150 s (Fig. 4). The results showed that magnitude of the peak current (I_p) increased with increasing potential in the range from −0.30 to 0.20 V. At more positive preconcentration potentials, a significant decrease in the magnitude of the peak current (I_p) was observed. Therefore, a preconcentration potential of 0.20 V was the best and was applied in the present analytical study.

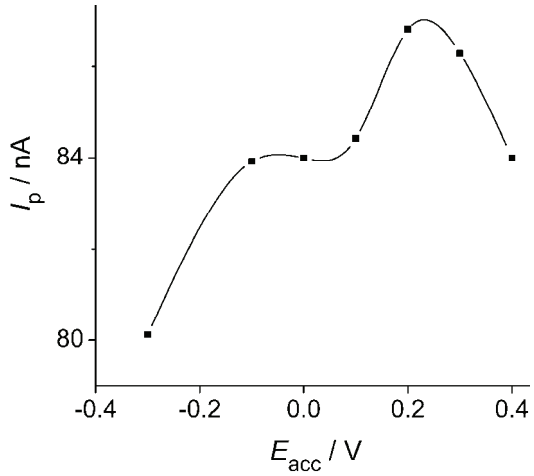


Fig. 4. Effect of preconcentration potential (E_{acc}) on the DPASV peak current (I_p) of 10.0 μg mL^{-1} berberine in acetate buffer (0.2 M, pH 5.6) after preconcentration onto a 5 mass % nano-Na-MMT/CPE for 150 s; ΔE_s = 6 mV, E_a = 100 mV, t_w = 0.1 s and t_p = = 0.5 s.

On the other hand, DPASV of 4.0 and 10.0 μg·mL^{-1} berberine were recorded at increasing preconcentration times (t_{acc}) under the foregoing optimal operational conditions. As shown in Fig. 5, in order to avoid the saturation of electrode surface, a preconcentration time of 150 s was applied in the present analytical study.

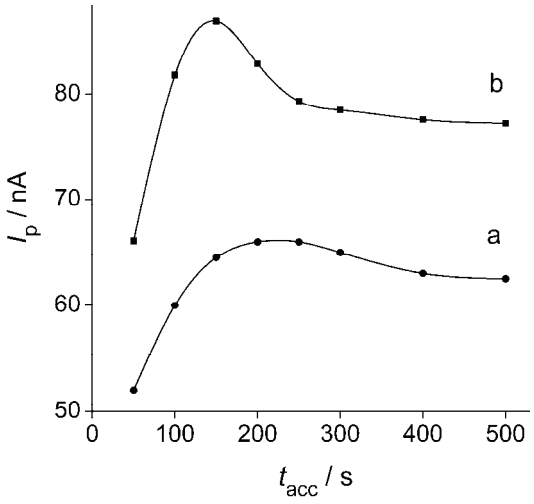


Fig. 5. Effect of preconcentration time (t_{acc}) on the DPASV peak current (I_p) of 4.0 (a) and 10.0 μg mL^{-1} (b) berberine in acetate buffer (0.2 M, pH 5.6) after preconcentration onto a 5 mass % nano-Na-MMT/CPE at 0.20 V; ΔE_s = 6 mV, E_a = 100 mV, t_w = 0.1 s and t_p = = 0.5 s.

According to the above results, the optimum operational conditions of the DPASV method utilizing 5 mass % nano-Na-MMT/CPE in acetate buffer (0.2 M, pH 5.6) were: E_{acc} = 0.20 V, t_{acc} = 150 s, ΔE_s = 6 mV, E_a = 100 mV, t_w = 0.1 s and t_p = 0.5 s.

Linearity

The relationship between the magnitude of the oxidation peak current (I_p) and the concentration of berberine (Fig. 6) was examined utilizing the developed 5 mass % nano-Na-MMT/CPE in acetate buffer (0.2 M, pH 5.6) by the developed DPASV method. A linear range from 1.0 to 18.0 μg mL^{-1} berberine was obtained with the following regression equation:

$$I_p \text{ (nA)} = 20.34c \text{ (μg mL}^{-1}\text{)} + 16.05 \ (r = 0.997 \text{ and } n = 6)$$

The limit of detection (*LOD*) and limit of quantification (*LOQ*) of berberine were estimated using the expression: kSD/b,[42] where k = 3 for the *LOD* and 10 for the *LOQ*, *SD* is the standard deviation of the blank and b is the slope of the calibration plot. The *LOD* and *LOQ* value were found to be 0.07 and 0.24 μg mL^{-1}, respectively.

Interference studies

The influence of various potentially interference species that are commonly found with berberine in pharmaceuticals on the determination of 10.0 μg mL^{-1} berberine were investigated to evaluate the selectivity of the proposed method. The tolerance limit was taken as the maximum concentration of the foreign substances that caused an approximately ±5 % relative error in the determination. The results after the experiments revealed that 800-fold of glucose, sucrose and citric acid, 500-fold of methanol, ethanol, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Fe^{2+}, NH^{4+},

PO_4^{3-}, SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, NO_3^-, Cl^- and F^-, 300-fold of potassium sorbate, aqueous ethylcellulose and carboxymethyl cellulose, 50-fold of Tween 60 and Tween 80, and a saturated starch solution did not affect the selectivity. Although ascorbic acid showed interference in the determination of berberine, the interference could be minimized, if necessary, by using the ascorbic oxidase enzyme, which exhibits high selectivity to the oxidation of ascorbic acid. These results confirmed the suitable selectivity of the proposed method for the determination of berberine.

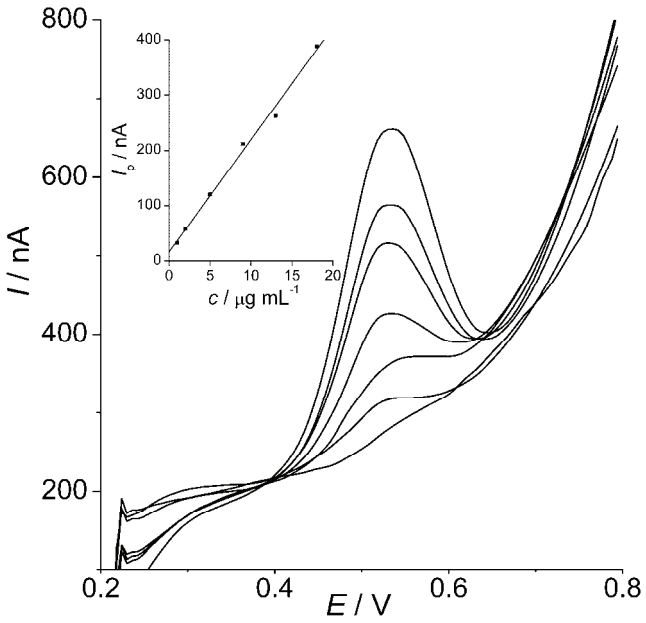


Fig. 6. DPASV recorded at a 5 mass % nano-Na-MMT/CPE for different concentration of berberine (1.0, 2.0, 5.0, 9.0, 13.0 and 18.0 μg mL^{-1}) in acetate buffer (0.2 M, pH 5.6). The inset shows a plot of peak current (I_p) *vs*. the concentration of berberine.

Analytical application

The sample powder was obtained from 10 tablets after the sugar-coating had been carefully removed. An accurately weighed amount of the power was dissolved in ultra pure water by ultrasonic sound for 30 min. After addition of an appropriate quantity of sample solution into 10 mL acetate buffer (0.2 M, pH 5.6), the DPASV was recorded.

The content of berberine was obtained by the standard addition method, and the results are listed in Table I. The recovery rates of standard solution of berberine were examined to detect the interference of excipients and co-formulated drugs. The value of recovery was at the range from 97.9 to 104.4 %, which

suggested that the excipients and co-formulated drugs have an acceptable interference on the determination. In addition, the average content of berberine in the selected tablets is 29.65 mg per tablet. The value of relative standard deviation and relative error were 1.02 and −1.16 %, respectively.

TABLE I. Results of berberine analysis in real samples (n = 5)

Sample	Detection result of sample μg mL^{-1}	Standard solution added μg mL^{-1}	Standard solution found μg mL^{-1}	Recovery %	Result of sample mg/tablet
1	9.785	5.000	5.220	104.4	29.64
2	9.659	5.000	5.119	102.4	29.26
3	9.746	5.000	4.965	99.3	29.52
4	9.824	5.000	5.050	101.0	29.76
5	9.932	5.000	4.893	97.9	30.08

CONCLUSION

In this work, a new method based on a nano-Na-montmorillonite clay modified carbon paste electrode was first developed for studying the direct electrochemical oxidation of berberine chloride. Simultaneously, a simple and sensitive differential pulse anodic stripping voltammetric method was developed and described in detail. This method was applied to the direct assay of berberine in pharmaceutical tablets without any precipitation, evaporation or extraction process, which were not necessary, as there was no interference from the excipients. The high precision, accuracy, sensitivity and selectivity of the method can foresee its promising application as a simple, convenient, and fast electrochemical method for the determination of berberine in clinical and pharmaceutical formulations.

Acknowledgements. The authors express their gratitude for the berberine drug provided by the College of Pharmacy of the Southwest University (Chongqing, China) and for the financial supports from the Doctor special fund for Basic Scientific Research of Southwest University (No. 104200-20710906).

ИЗВОД

ОДРЕЂИВАЊЕ БЕРБЕРИНА ДИФЕРЕНЦИЈАЛНОМ ПУЛСНОМ АНОДНОМ СТРИПИНГ ВОЛТАМЕТРИЈОМ НА ЕЛЕКТРОДИ ОД УГЉЕНИЧНЕ ПАСТЕ МОДИФИКОВАНЕ НАНОЧЕСТИЦАМА НАТРИЈУМ-МОНТМОРИЛОНИТА

WEN CHEN, MING-XIAO ZHANG, CONG LI и YONG-LING LI

School of Chemistry and Chemical Engineering, Southwest University, 2 Rd Tiansheng, Beibei District, Chongqing, P. R. China

Представљена је једноставна и осетљива електрохемијска метода одређивања берберина на електроди од угљеничне пасте модификоване наночестицама натријум-монтморилонита. На овој електроди је испитивана електрохемијска оксидација и адсорпција берберина помоћу волтаметрије са линеарно променљивим потенцијалом у ацетатном пуферу (0,2 M и pH 5,6). Развијена је процедура одређивања поменутог лека методом

диференцијалне пулсне анодне стрипинг волтаметрије. Добијена је добро дефинисана линеарна зависност максимума струје оксидације берберина од његове концентрације у опсегу од 1,0 до 18,0 μg mL^{-1} са границом детекције од 0,24 μg mL^{-1}. Предложена метода је успешно примењена за одређивање берберина у комерцијалним таблетама.

(Примљено 27. маја, ревидирано 16. јула 2012)

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